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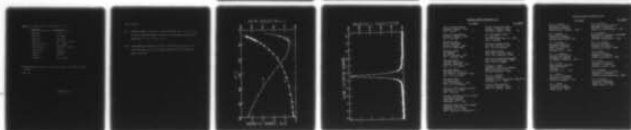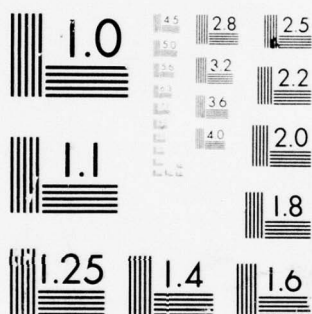   DEC 77   J T WROBLESKI, D B BROWN   N00014-75-C-0756
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TECHNICAL REPORT. NO. 7

Physical and Chemical Properties of Squarate Complexes. I. Spectral,
Magnetic, and Thermal Behavior of Dimeric Iron(III) Squarate.

by

James T. Wrobleski and David B. Brown*

Prepared for Publication

in the

Inorganic Chemistry

University of Vermont

Department of Chemistry

Burlington, Vermont 05401

December 8, 1977

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The magnetic susceptibility behavior of an iron(III) squarate complex with empirical formula $Fe(C_4O_4)(OH)(H_2O)_3$ has been studied in the range 20-300K. These susceptibilities were best fit to a $S_1=S_2=5/2$ dimer model with $J=-6.9$ cm^{-1} and g=2.00. Presence of both terminally-coordinated bidentate squarate dianion and bridging hydroxy groups is supported by the infrared spectrum of the dimer. The ^{57}Fe Mössbauer spectrum of this compound consists of a single absorption with δ=0.40 mm/s relative to iron metal. Based on these

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results an octahedral structure with molecular formula $[Fe(C_4O_4)(OH)(H_2O)_2]_2 \cdot 2H_2O$ is suggested for this dimer. The thermal weight loss curve for this material is described by the initial loss of both lattice and coordinated water followed by a complex decomposition process involving the squarate ligand.

Physical and Chemical Properties of Squarate Complexes. I. Spectral,
Magnetic, and Thermal Behavior of Dimeric Iron(III) Squarate

by

James T. Wrobleski and David B. Brown*

Contribution from the Department of Chemistry
University of Vermont, Burlington, Vermont 05401

Trivalent metal-ion complexes which contain the squarate dianion (I, Sq) with general formula $M(Sq)(OH)(H_2O)_3$ were first reported by West and Niu[1] (M=Aℓ, Cr, or Fe) and Condren and McDonald[2] (M=V). Niu's suggestion of a dimeric structure for

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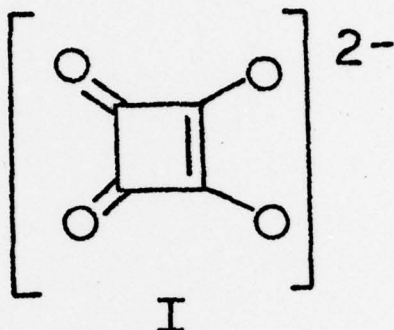
$Fe(Sq)(OH)(H_2O)_3$ was principally supported by the reduced room temperature magnetic moment of this compound. The other trivalent metal complexes were subsequently assigned dimeric structures based on their x-ray isomorphism to the iron compound.[1,2]

As part of our investigation of the electronic and structural properties of iron-squarate complexes we have studied the variable-temperature magnetic susceptibility, spectral, and thermal behavior of $Fe(Sq)(OH)(H_2O)_3$, and report here evidence which supports a dihydroxy-bridged dimeric structure (II) for this complex.

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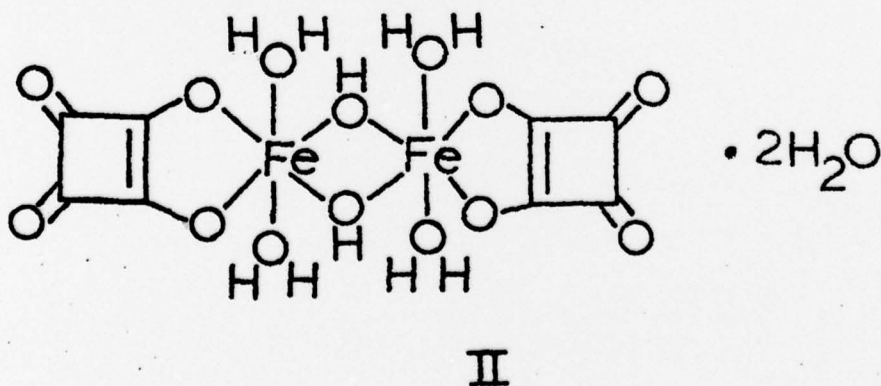
Experimental Section

Materials and Methods. Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) was purchased from Aldrich Chemical Co. and used as received. $FeCl_3 \cdot 6H_2O$ was purified by centrifuging a concentrated ethanolic solution of commercial hydrated ferric chloride and discarding the insoluble material. Magnetic susceptibilities were determined using a conventional Faraday balance calibrated with $Hg[Co(NCS)_4]$.[4] Ligand diamagnetism was treated as usual by assuming $X_{sq} = 30.6 \times 10^{-6}$ cgsu[1] and by using a table at Pascal's constants.[5] Mössbauer spectra were obtained by using the spectrometer previously described[6] with a $^{57}Co(Pt)$ source maintained at room temperature. A moderately-thin foil of natural α-Fe was used to define the velocity scale. Mössbauer spectra were deconvoluted by assuming pure Lorentzian line shapes superimposed on a parabolic base line. Parameters obtained in this manner were reproducible to ± 1%. Infrared spectra were obtained on a Beckman IR 20A instrument by using KBr pressed pellets. X-ray powder diffraction patterns were obtained with the Straumanis technique by using vanadium-filtered Cr radiation ($\lambda_{mean} = 2.2909Å$). TGA curves were obtained by using a Dupont 900 Thermal Analyzer coupled to a Dupont 950 Thermogravimetric Analyzer. Iron was determined by EDTA titrimetry. C and H analyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Preparation of $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$. Di[μ-hydroxodiaquosquaratoiron(III)] dihydrate was prepared by adding an ethanolic solution of $FeCl_3$ to a stoichiometric amount of squaric acid dissolved in hot water. The resulting purple solution was refluxed and filtered. Upon cooling a purple-brown material crystallized. This solid was collected, repeatedly washed with cold ethanol, and air dried at room temperature. Anal. Calcd for $FeC_4H_7O_8$: Fe, 23.38; C, 20.11; H, 2.95. Found: Fe, 23.6; C, 19.93; H, 2.84. A partially deuterated analog was prepared by using 90% D_2O as reaction solvent. X-ray powder patterns of the normal and deuterated materials were identical.

Results and Discussion

X-ray powder pattern d-spacings obtained for the samples of $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$
prepared in this study are identical to those reported by West and Niu[1]. Magnetic
susceptibility data for $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$ given in Table I[7] and shown in
Figure 1 indicate moderate intramolecular antiferromagnetic spin exchange in this
material. Both the magnitude and temperature dependence of the susceptibility typify
the behavior of an $S_1 = S_2 = 5/2$ dimer.[8] For such a system the following expression
for the susceptibility is obtained from the dipolar coupling approach of Van Vleck.[9]

$$X_M = \frac{2N\beta^2 g^2}{kT} \left[\frac{55 + 30\exp(-10J/kT) + 14\exp(-18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT)}{11 + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)} \right]$$

Symbols in this expression have their usual meanings. A least squares fit of the
experimental susceptibility to this equation yields values of J and g. By assuming
$g = 2.00$, the smooth curves shown in Figure 1 are obtained for $J = -6.9$ cm^{-1}. This
value of $|J|$ is inconsistent with both oxo- and squarato-bridged structures. Oxo-bridged
Fe(III) dimers are invariably characterized by coupling constants near -100 cm^{-1}.[10]
Squarate bridges, on the other hand, provide a poor exchange path as experimentally
observed for the polymers $Ni(Sq)(H_2O)_2$ ($J = -0.7$ cm^{-1})[11] and $Fe(Sq)(H_2O)_2$ ($J \sim -0.7$ cm^{-1})[12]
and the dimers $[Cu_2(Et_5 dien)_2(Sq)](BPh_4)_2$ ($J = -2.1$ cm^{-1})[13] and $[Ni_2(macro)_2(Sq)]$
$(ClO_4)_2$ ($J = -0.4$ cm^{-1}).[14] Coupling constants in the vicinity of -10 cm^{-1} have been
observed for several dibridged Fe(III) dimers, including dihydroxo-bridged dimers.[15,16]

A room temperature Mössbauer spectrum of $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$, shown in
Figure 2 , may be described by a single Lorentzian line with isomer shift $\delta = 0.40$ mm/s.

If the data are fit to a quadrupole doublet, a splitting of $\Delta = 0.16$ mm/s is obtained with $\delta = -0.40$ mm/s, $\Gamma_1 = 0.40$, and $\Gamma_2 = 0.38$ mm/s. The fit is essentially identical for these two sets of parameters. Although the isomer shift increases to 0.48 mm/s at 19K we do not observe any greater resolution of the quadrupole doublet at low temperature.

Small values of Δ, taken by themselves, do not distinguish tetrahedral from octahedral coordination for Fe(III) nor do they differentiate low-spin Fe(II) from high-spin Fe(III).[17] In general the same applies for δ. Spin state is fortunately easy to diagnose from susceptibility data, but it is more difficult to distinguish T_d from O_h coordination for Fe(III). It has been our general experience that in the absence of magnetically-perturbed Mössbauer data (which may be equivocal for small Δ), it is possible to make this distinction by considering the relative percent effect (percent transmission) of T_d Fe(III) complexes to O_h Fe(III) complexes. Whereas many $[FeX_4]^-$ complexes show 1-2% effect at room temperature, octahedral Fe(III) compounds at the same temperature realize 10-20% effect. This argument is by no means unequivocal but may be used as a qualitative guide in many instances. The relatively high percent effect shown by $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$ at RT (Figure 2) would seem to support octahedral rather than tetrahedral Fe(III) in this compound.

Infrared spectra of squarate-containing compounds are quite characteristic of the mode of coordination.[2] Thus it is possible to distinguish the terminal form of squarate as in II from the bridging form by virtue of the lower symmetry of the former. Polymeric divalent metal squarates, which contain the squarate ion in approximately D_{4h} symmetry, have as the most prominent feature in their infrared spectra a broad band near 1500 cm^{-1} assigned to a mixture of C-O and C-C stretching modes.[1,2,12] The infrared spectrum of $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$ however shows not only this absorption but also moderate bands at 1640 and 1815 cm^{-1}. The former absorption may be assigned

to a C=C stretching mode and the latter to a C=O stretching mode. The infrared spectrum of this complex thus suggests nominal $\underline{C}_{2v}$ symmetry for the squarate ion, as in squaric acid and metal squarates involving bidentate coordination of the squarate ion. A number of other infrared absorptions are present in the spectrum of $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$, all of which are consistent with structure II.[18] These bonds and appropriate assignments are listed in Table II. We have assigned a weak absorption at 850 cm^{-1} to the Fe-O-H deformation mode associated with bridging hydroxo groups.[15] This assignment is supported by the observation that this band decreases in intensity upon partial deuteration.

The thermal weight loss curve of $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$ obtained in a nitrogen atmosphere shows two inflections. The first, at 160°C, corresponds to a 17.3% weight loss and the second, at 290°C, corresponds to a 64.8% total weight loss. If the first step corresponds only to dehydration then 4.6 moles of water are lost per mole of dimer. An x-ray powder pattern of the final residue shows the presence of iron metal. The total theoretical weight loss is 66.6% if iron metal is the only product of the decomposition. The thermal behavior of this material contrasts markedly with that of the vanadium analog.[2] The vanadium complex loses two moles of water per dimer at 80° in vacuum, and six moles of water in either air or argon at ca 150°, and, ultimately, decomposes to vanadium oxides, rather than the metal, at higher temperatures. The complexity of the final decomposition step in these complexes has been previously noted both for divalent[19,20] and trivalent[2] metal squarates.

Supplementary Material Available: A listing of observed magnetic susceptibilities Table I (1 page). Ordering information is given on any current masthead page.

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Table I. Magnetic Susceptibilities and Moments [a]

T,K	X_M', cgsu	$\mu eff/Fe, \mu_B$	μ_{calc}, μ_B
21.8	0.04054	1.88	1.92
22.1	0.04172	1.92	1.94
23.2	0.04141	1.96	2.00
24.2	0.04216	2.02	2.05
26.3	0.04395	2.15	2.15
27.8	0.04433	2.22	2.22
29.2	0.04571	2.31	2.28
31.8	0.04417	2.37	2.39
33.5	0.04554	2.47	2.46
34.3	0.04630	2.52	2.50
36.2	0.04598	2.58	2.57
39.0	0.04719	2.71	2.68
46.2	0.04710	2.95	2.93
55.0	0.04656	3.20	3.21
68.5	0.04600	3.55	3.57
82.1	0.04538	3.86	3.87
96.1	0.04460	4.14	4.12
104.2	0.04314	4.24	4.24
126.0	0.04037	4.51	4.50
146.7	0.04750	4.69	4.69
165.5	0.03523	4.83	4.83
196.2	0.03199	5.01	5.00
223.2	0.02924	5.11	5.11
247.6	0.02731	5.20	5.19
266.6	0.02576	5.24	5.24
285.8	0.02439	5.28	5.30
296.7	0.02385	5.32	5.31

[a] $X' = 150 \times 10^{-6}$ cgsu.

Table II.   Infrared Bands and Assignments (in cm^{-1}) [a]

Absorption	Assignment
3200 br, s	$\nu(OH)$
1815 sh, m	$Sq, \nu(C=O)$
1640 sh, m	$Sq, \nu(C=C)$
1500 br, s	$Sq, \nu(C-C) + \nu(C-O)$
1110, 1085 sh, w	Sq, ν_{13}, E_u [b]
850, 750 br, w	$\nu(Fe-O-H) + \rho_r(H_2O)$
660, 460 br, w	$\rho_w(H_2O)$
420 sh, w	unassigned
390 sh, w	$\nu(Fe-O)$
350 sh, vw	Sq, ν_2, A_{1g} [b]

[a] Abbreviations: br, broad; s, strong; sh, sharp; m, moderate; w, weak; v, very.

[b] Ref 18.

Figure Captions

Fig. 1 Effective magnetic moments for $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$. The solid line
gives the theoretical moments obtained for an exchange-coupled $S_1 = S_2 = 5/2$
dimer with $J = -6.9$ cm^{-1} and $g = 2.00$.

Fig. 2 Room temperature Mössbauer spectrum of $[Fe(Sq)(OH)(H_2O)_2]_2 \cdot 2H_2O$. The
solid line gives the fit for a single Lorentzian line with parameters
given in the text.

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